

Conformational Entropy of Compact Polymers

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Exact results for the scaling properties of compact polymers on the square lattice are obtained from an effective field theory. The entropic exponent $\gamma = 117/112$ is calculated, and a line of fixed points associated with interacting chains is identified; along this line γ varies continuously. Theoretical results are checked against detailed numerical transfer matrix calculations, which also yield a precise estimate for the connective constant $\kappa = 1.47280(1)$.

Polymers are long, flexible molecules, and as such their conformations are well described by different types of random walks [1]. For example, polymers in good solvents are modeled by self-avoiding random walks which can be mapped to a magnetic system at the critical point. This mapping leads to controlled approximate calculations for conformational exponents ν and γ in three dimensions [1], and exact results in two [2]. These exponents describe the power-law dependence of the linear size, and of the conformational entropy, on the number of monomers, respectively.

Unlike polymers in good solvents which are swollen, globular proteins in their native state form compact structures. On the lattice, compact polymers are modeled by Hamiltonian walks, i.e., self-avoiding walks that visit *all* the sites.

Recently, compact polymers on two and three-dimensional lattices have become the model of choice for protein folding studies [3]. Here the focus is on the effect of non-specific and non-local hydrophobic interactions among the amino acids, on the folding process, and on the formation of secondary structure (helices and sheets). These investigations have been almost exclusively numerical, and an analytical theory of protein conformations that takes into account self-avoidance and compactness, as well as specific sequence information, would be of considerable interest [3]. As a first step towards this goal we construct a field theory of compact polymers on the two-dimensional square lattice which provides detailed and exact information about their conformational statistics.

Conformational exponents for compact polymers on the *honeycomb* lattice were calculated recently using Bethe Ansatz techniques [4]. Since there is a certain degree of frustration associated with the Hamiltonian con-

straint one might expect the exponents to change from one type of lattice to another. Namely, the number of *contacts*, i.e., monomer pairs which are not adjacent along the chain but occupy nearest neighbor positions on the lattice, is *one* per monomer on the honeycomb, and *two* per monomer on the square lattice. Since hydrophobic interactions in lattice models of proteins occur at contacts, the square and honeycomb problem describe different physical situations.

Here we present for the first time exact results for compact polymers on the square lattice. From numerical transfer matrix calculations it was already observed that $\gamma = 1.0444(1)$ [5] differs from the honeycomb value $\gamma = 1$; the latter was also the outcome of a mean-field calculation [6]. We find $\gamma = 117/112 = 1.0446\dots$. Furthermore, we describe a *line* of fixed points associated with interacting compact polymers, along which γ varies continuously. These results are in excellent agreement with our numerical transfer matrix calculations, which also provide a very precise estimate of the connective constant, $\kappa = 1.47280(1)$. This constant describes the leading, exponential scaling of the number of compact polymer conformations (\mathcal{C}) with the number of monomers: $\mathcal{C} \sim \kappa^N$.

Our identification of compact polymers with a *critical* model also has bearings on the cooperativity of protein folding thermodynamics [3]. Namely, since there is no energy gap separating the first excited (non-compact) state from the native (compact) ones, at least in the large chain limit, we conclude that homopolymer collapse is a one-state process [3].

a. Loop model To construct a field theory of compact polymers we make use of the two-flavor fully packed loop (FPL²) model on the square lattice [7,8]. It plays the role of the $O(n)$ loop model [2] from which exact results for

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swollen and dense polymers were derived. The polymer problem is recovered from the loop model in the limit of vanishing fugacity for one of the loop flavors.

The allowed loop configurations (\mathcal{G}) of the FPL² model are defined by drawing (*black*) loops along the bonds of the square lattice with the constraint that each site is covered by exactly one loop. Loops are not allowed to cross and each is assigned a fugacity n_b . The bonds not covered by loops also form (*gray*) loops whose number (N_g) is *not* constrained by the number of black loops (N_b). Gray loops do not intersect, and each is assigned a fugacity n_g . The partition function of the FPL² model is

$$Z = \sum_{\mathcal{G}} n_b^{N_b} n_g^{N_g} . \quad (1)$$

The FPL² model is the first loop model studied to date that possesses a *two-dimensional* manifold of critical fixed points, for $0 \leq n_b, n_g \leq 2$ [9]; $n_b \rightarrow 0$ is the compact polymer problem. From here on we focus on the critical region of the phase diagram, for which exact results were previously obtained only along the line of special symmetry, $n_b = n_g$ [8].

b. Height model For the FPL² model we construct an effective field theory by mapping it to an interface model. The basic idea is to interpret the loops as contour lines of a height [2]. First we orient the loops independently and randomly, so as to be able to decide in which direction the height increases. Given an oriented loop configuration the microscopic heights \mathbf{z} are defined at the centers of the lattice plaquettes. Each bond is in one of four states, labeled by *vectors* **A**, **B**, **C** or **D**, depending on its flavor and direction. Starting from an even site an oriented black (gray) loop is defined as a sequence **ABAB**... (**CDCD**...) of bond states. The *increase* in \mathbf{z} , when going *clockwise* around an even site, is **A**, **B**, **C** or **D** depending on the state of the bond being crossed. The fully packing constraint implies that all four bond states are represented at every site, hence, in order for the height to be well defined, we must have **A**+**B**+**C**+**D**=0. The four vectors thus span a three-dimensional vector space which is the space of heights. We adopt the normalization of Ref. [7]: **A** = (-1, +1, +1), **B** = (+1, +1, -1), **C** = (-1, -1, -1), and **D** = (+1, -1, +1)

To complete the mapping from loops to heights we must specify the way in which the fugacities n_b and n_g are distributed between the two possible orientations. The clockwise oriented black loops are assigned the weight $\exp(i\pi e_b)$, and similarly for the gray loops with e_g replacing e_b . The anti-clockwise loops are weighted with the opposite phase. This way, summing over the two orientations, for any given loop produces the original fugacities:

$$n_b = 2 \cos(\pi e_b) , \quad n_g = 2 \cos(\pi e_g) . \quad (2)$$

The reason for choosing to redistribute the loop fugacity in this fashion is that it allows for a *local* definition of oriented loop weights, which ultimately leads to a local effective field theory. In particular, if we assign to every right turn of an oriented black loop the weight $\lambda_b = \exp(i\pi e_b/4)$, and λ_b^{-1} for a left turn, then the whole loop will be weighted correctly, since the difference in the number of right and left turns for a closed loop on the square lattice is ± 4 . The rule for the gray loops is the same with e_g replacing e_b . This assigns to each vertex of the square lattice a weight $\lambda(\mathbf{x})$ which is the product of the local weights associated with the oriented black and gray loop passing through \mathbf{x} .

Once the height at the origin is fixed, oriented loop configurations are in a one to one correspondence with height configurations which acquire their weights. Coarse-graining of the microscopic heights produces the height field $\mathbf{h}(\mathbf{x})$ whose fluctuations are described by a conformally invariant Liouville field theory.

c. Liouville theory The effective field theory for the coarse grained heights is given by the Euclidean action

$$S = S_E + S_B + S_L \quad (3)$$

where each of the three terms

$$S_E = \frac{1}{2} \int d^2\mathbf{x} K_{\alpha\beta} \partial h^\alpha \cdot \partial h^\beta \quad (4)$$

$$S_B = \frac{i}{4\pi} \int d^2\mathbf{x} (\mathbf{e}_0 \cdot \mathbf{h}) \mathcal{R} \quad (5)$$

$$S_L = \int d^2\mathbf{x} \sum_{\mathbf{e} \in \mathcal{R}_w^*} \tilde{w}_{\mathbf{e}} \exp(i\mathbf{e} \cdot \mathbf{h}(\mathbf{x})) , \quad (6)$$

has a concrete geometrical interpretation.

The first, *elastic term*, accounts for the entropy of oriented loop configurations. The symmetries of the oriented loop model impose constraints on the stiffness tensor \mathbb{K} : $K_{11} = K_{33}$ and $K_{12} = K_{23} = 0$ [9]. We thus find *three* elastic constants which are not related by symmetry. This is in contrast to all previously solved loop models which are characterized by a single coupling constant [2].

The second, *boundary term*, describes the coupling of the height field to the scalar curvature \mathcal{R} . We are only concerned with the FPL² model defined on flat lattices for which \mathcal{R} is zero everywhere except possibly at the boundary. For example, on the cylinder $\mathcal{R} = 4\pi[\delta(\infty) - \delta(-\infty)]$, and S_B has the effect of inserting vertex operators $\exp(\pm i\pi \mathbf{e}_0 \cdot \mathbf{h})$ at the two far ends. These vertex operators supply *winding* loops with the weight $\exp[i\pi \mathbf{e}_0 \cdot (\mathbf{h}(\infty) - \mathbf{h}(-\infty))]$, since these are the only loops that contribute to the height difference between the two far ends. This extra phase factor is necessary, for a winding loop has an equal number of left and right turns, implying that the local vertex weights would assign it a total weight of 1, regardless of direction or flavor. For S_B to correct this, the *background charge* must be

$$\mathbf{e}_0 = -\frac{\pi}{2}(e_g + e_b, 0, e_g - e_b). \quad (7)$$

The third term, the so-called *Liouville potential*, is the coarse-grained version of the microscopic weight, $\prod_{\mathbf{x}} \lambda(\mathbf{x})$, assigned to an oriented loop configuration. If we define $w(\mathbf{x}) = -\ln(\lambda(\mathbf{x}))$, then the operator $w(\mathbf{x})$ is invariant under translations in height space that form the bcc lattice \mathcal{R}_w . As such it can be expanded in a Fourier series, Eq. (6), where the electric charges \mathbf{e} take their values in the reciprocal lattice \mathcal{R}_w^* ; \mathcal{R}_w^* is an fcc lattice with a conventional cubic cell of side 2π [9].

The three elastic constants appearing in the action completely determine the scaling dimensions of all operators constructed from the height. Apart from the afore-mentioned vertex operators there are also defect operators which correspond to *vortex* configurations of the height. Vertex operators are defined by the electric charge \mathbf{e} while defect operators are characterized by the magnetic charge \mathbf{m} , which is the height mismatch around the vortex core. The scaling dimension of a general operator with both electric and magnetic charge [10] is

$$x(\mathbf{e}, \mathbf{m}) = \frac{1}{4\pi} \mathbf{e} \cdot [\mathbb{K}^{-1} \cdot (\mathbf{e} - 2\mathbf{e}_0)] + \frac{1}{4\pi} \mathbf{m} \cdot [\mathbb{K} \cdot \mathbf{m}]; \quad (8)$$

\mathbb{K} is the stiffness tensor in Eq. (4).

To calculate the three elastic constants that make up \mathbb{K} we turn to the *loop ansatz* [8], which states that the Liouville potential is marginal, i.e., the most relevant (in the RG sense) vertex operators appearing in the sum in Eq. (6) have dimension $x(\mathbf{e}, 0) = 2$. There are four such vertex operators among the twelve shortest vectors in \mathcal{R}_w^* : $(-\pi, 0, \pm\pi)$ and $(-\pi, \pm\pi, 0)$. Using Eq. (8) this leads to four equations for the three elastic constants with the unique solution:

$$\begin{aligned} K_{11} &= \frac{\pi}{8} (2 - e_b - e_g), \\ K_{13} &= \frac{\pi}{8} (e_b - e_g), \\ K_{22} &= \frac{\pi}{2} \frac{(1 - e_b)(1 - e_g)}{2 - e_b - e_g}. \end{aligned} \quad (9)$$

d. Conformational exponents Points in the critical region of the FPL² model are characterized by the central charge and the geometrical scaling dimensions x_{s_b, s_g} , which are both functions of the loop fugacities n_b and n_g . The central charge provides information about the finite-size corrections to the free energy, while the scaling dimensions are defined by the asymptotic relation $Z_{s_b, s_g}(\mathbf{0}, \mathbf{r})/Z \sim |\mathbf{r}|^{-2x_{s_b, s_g}}$; $Z_{s_b, s_g}(\mathbf{0}, \mathbf{r})$ is the partition function of the FPL² model with the constraint that there are s_b black and s_g gray strings connecting points $\mathbf{0}$ and \mathbf{r} ; see Fig. 1. We consider the two end points to be in the bulk, in which case $s_b + s_g$ is necessarily even; the odd case is associated with boundary operators [9].

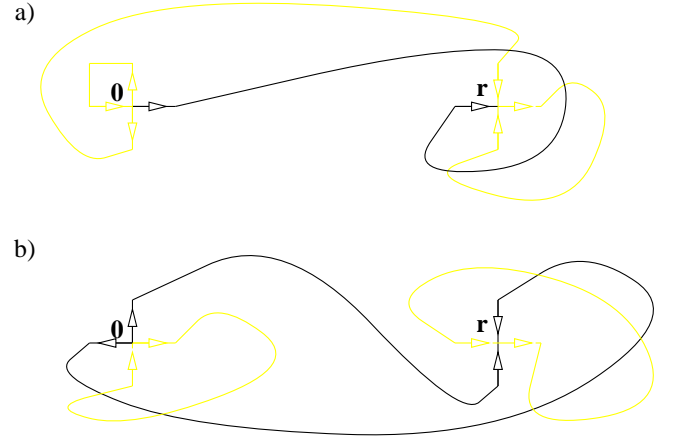


FIG. 1. Defect configurations used for calculating geometrical scaling exponents $x_{1,1}$ (a) and $x_{2,0}$ (b). Bond states around point $\mathbf{0}$, listed clockwise from the leftmost bond, are **DCAC** (a) and **AACD** (b).

The central charge of the Liouville field theory is [10]

$$c = 3 + 12x(\mathbf{e}_0, 0) = 3 - 6 \left(\frac{e_b^2}{1 - e_b} + \frac{e_g^2}{1 - e_g} \right). \quad (10)$$

In Table I we compare this formula with numerical transfer matrix calculations along the compact polymer line ($n_b = 0$, $e_b = 1/2$) and excellent agreement is found. This holds true for the *whole* critical region [9].

Here we are interested in the conformational exponents γ and ν for compact polymers [11], and so it suffices to calculate the geometrical scaling dimensions $x_{1,1}$ and $x_{2,0}$ [12]. The formula for the whole spectrum x_{s_b, s_g} is a simple generalization of the calculation presented below [9].

To calculate $x_{1,1}$ we consider the diagram in Fig. 1a which represents an FPL² configuration with a single black and a single gray string connecting the two points separated by \mathbf{r} . In the height representation these configurations are associated with topological defects with charges $\pm \mathbf{m}_{1,1}$ placed at the two points; $\mathbf{m}_{1,1} = \mathbf{C} - \mathbf{B} = (-2, -2, 0)$ is the net height change upon encircling the point $\mathbf{0}$. Since an oriented segment is weighted by a complex phase, whose value depends on the number of times the string winds around $\mathbf{0}$ and \mathbf{r} , vertex operators with charge \mathbf{e}_0 have to be inserted at both points in order to weight all segments equally [2]. Therefore, $x_{1,1}$ is the dimension of an operator with total charge $(\mathbf{e}_0, \mathbf{m}_{1,1})$, and

$$\begin{aligned} 2x_{1,1} &= \frac{1}{4} [(1 - e_b) + (1 - e_g)] \\ &+ \frac{(1 - e_b)(1 - e_g)}{(1 - e_b) + (1 - e_g)} - \left[\frac{e_b^2}{1 - e_b} + \frac{e_g^2}{1 - e_g} \right] \end{aligned} \quad (11)$$

follows from Eqs. 8 and 9.

Similarly the diagram Fig. 1b leads to the result:

$$2x_{2,0} = 2x(\mathbf{e}_b, \mathbf{m}_{2,2}) = (1 - e_b) - \frac{e_b^2}{1 - e_b}. \quad (12)$$

In this case point $\mathbf{0}$ serves as a source of two black strings, and therefore corresponds to a topological defect of strength $\mathbf{m}_{2,2} = \mathbf{A} - \mathbf{B} = (-2, 0, 2)$. The electric charge $\mathbf{e}_b = -\pi/2(e_b, 0, -e_b)$ now compensates for the extraneous phase factors due to the windings of the black loop segments only, since no gray segments connect the two points.

Our main results follow from Eqs. (11)–(12) and the scaling relations $\gamma = 1 - x_{1,1}$ and $1/\nu = 2 - x_{2,0}$ [12]. For compact polymers $\gamma = 117/112$ is obtained by setting $e_b = 1/2$ ($n_b = 0$) and $e_g = 1/3$ ($n_g = 1$) in Eq. (11). The fact that $x_{1,1} < 0$ indicates an effective repulsion between the chain ends. This is to be contrasted to the mean-field result $\gamma = 1$, also found for compact polymers on the honeycomb lattice [4], which implies that the chain ends are uncorrelated. Hitherto numerical studies based on enumerations of short compact polymer conformations [13] have failed to provide the accuracy needed to distinguish γ from its mean-field value.

Examination of Eq. (11) reveals a novel feature of compact polymers on the square lattice. Namely, allowing n_g to take different values along the $n_b = 0$ line represents a situation where different conformations are weighted differently depending on the number of gray loops present. In the critical region of the FPL² model each of these weighted compact polymer problems defines a different critical geometry characterized by a continuously varying γ . Similar behavior was predicted for directed self-avoiding walks with orientation dependent contact interactions [14].

Finally, from Eq. (12) we obtain the conformational exponent $\nu = 1/(2 - x_{2,0}) = 1/2$, independent of n_g . This result serves as a nice consistency check on our theory since compact structures have Hausdorff dimension $D = 2$ regardless of how they are weighted, and $\nu = 1/D$.

e. Numerical results To check our results we have constructed transfer matrices in a connectivity basis analogous to that of the $O(n)$ model [15], but taking into account the additional flavor information of the FPL² model [9]. The various sectors containing 0, 1 and 2 strings were considered for strip widths up to $L = 14$. Conformal invariance was used to relate the finite-size corrections of the eigenvalue spectra to the central charge and various geometrical scaling dimensions. Results along the compact polymer line are shown in Table I; agreement with theory is excellent, apart from discrepancies for $x_{1,1}$ at $n_g = 2$ which we attribute to logarithmic corrections. An extrapolation scheme based on the exact values of c , Eq. (10), yielded very precise estimates of the connective constant κ . Like γ , κ for $n_g = 1$ differs slightly from its mean-field value $4/e = 1.4715\dots$ [6], revealing the entropic origin of the effective repulsion between chain ends. Furthermore, κ changes continuously with the interaction-like parameter n_g .

n_g	0.0	0.5	1.0	1.5	2.0
c	-3.004(5)	-1.815(3)	-0.998(2)	-0.411(2)	-0.002(3)
(10)	-3	-1.8197...	-1	-0.4124...	0
$x_{1,1}$	-0.2500(3)	-0.1313 (9)	-0.0439(9)	0.0255(9)	0.0839(5)
(11)	-0.25	-0.1323...	-0.0446...	0.0260...	0.1042...
$x_{2,0}$	0.0000(0)	0.0000(0)	0.0000(0)	0.0000(0)	0.0000(0)
(12)	0	0	0	0	0
κ	1.41422(2)	1.44477(1)	1.47280(1)	1.49896(1)	1.52371(1)

TABLE I. Numerical results for the central charge c , geometrical exponents $x_{1,1}$ and $x_{2,0}$, and the connective constant κ along the line $n_b = 0$. Comparison is made to predictions from Eqs. (10), (11) and (12).

In conclusion, we have constructed a field theory of compact polymers on the square lattice from which exact results regarding their scaling properties were obtained for the first time. We hope that this might serve as a first step towards an analytic theory of simple lattice models of globular proteins [3].

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